

TECHNOLOGICAL AND ENVIRONMENTAL ASPECTS OF UTILIZATION OF HYDROLYSIC SULFURIC ACID OF PRODUCTION OF PIGMENT TITANIUM DIOXIDE

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Ukraine is one of the five countries producing strategic titanium raw materials. Testing of titanium objects from the standpoint of complexity will ensure their rational development and significantly increase profitability. The country has 40 deposits, of which: 1 – unique, 13 – large, 12 – prospected, 5 – developed. The deposits of titanium ores with commercial reserves have been explored since several decades. Other deposits reserve resources have been estimated in advance and constitute, conditionally, the "titanium reserves base of the country". At the same time, the total reserves and the reserve base of titanium ores of Ukraine, according to their estimates, "exceed those of any other country in the world."

Industrial titanium extraction is mainly produced from ilmenite – FeTiO_3 (36.8% iron, 31.6% oxygen, 31.6% titanium) and rutile – TiO_2 (60% titanium, 40% oxygen). «Sumykhimprom» annually consumes up to 150 thousand tons of ilmenite concentrate and produces 45 thousand tons of titanium dioxide by sulphate technology. At 1 ton of TiO_2 3.5 tons of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 1 ton $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and 9–10 tons of hydrolytic acid with the content of 15–18% of H_2SO_4 are formed.

Hydrolytic acid can not be reused in the production cycle of titanium dioxide. The suspensions of titanium hydroxide present in it can lead to premature hydrolysis of the solution. The main direction of its utilization is the evaporation to a concentration of 55% with subsequent use for the production of superphosphate. The costs of processing and neutralizing hydrolytic acid may exceed 30% of all production costs.

Considering that about 10 million tons of solutions of hydrolytic acid are produced annually in the world, the need to develop and introduce fundamentally different technological processes of acid regeneration becomes obvious.

A promising technology for utilization of waste – hydrolysis sulfate acid is the oxidation of iron(II) compounds to produce sulfuric solutions of iron(III) compounds. The best oxidizer of Fe^{2+} compounds, based on its availability, low cost and the absence of negative effects on further technological processes, is air oxygen. The disadvantage of the process of oxidizing Fe^{2+} with air oxygen is that this process is realized at elevated temperatures. However, the introduction of nitric acid or oxygen compounds of nitrogen, products of its decomposition, which act as a catalyst in the solution of Fe^{2+} , allows efficient oxidation at 25–50 °C.

Iron (III) compounds can be used as an oxidizing agent, at atmospheric pressure, what allows to use simpler and less expensive instrumentation for technological processes. In acidified ferric sulfate solutions can be dissolved chalcocite (Cu_2S), covetal (CuS), bornitis (Cu_5FeS_4), chalcopyrite (CuFeS_2) and sphalerite (ZnS). This makes it possible to consider water-soluble compounds of ferric iron as one of the most industrially acceptable effective oxidants.

This paper presents the results of a study of the effect of physicochemical, hydrodynamic factors and temperature on the rate of oxidation of Fe^{2+} ions by air oxygen in the presence of catalytic amounts of nitrogen oxides. The orders of oxidation reactions of Fe^{2+} over NO in the gas diffusion film and in solution were determined and amounted 1.9 and 1.06 respectively. And also, the value of the rate constant of oxidation of Fe^{2+} in solution, which becomes $0.9 \cdot 10^6 \text{ M}^{-2} \text{ c}^{-1}$. A mathematical model has been developed. This model makes it possible to give practical recommendations on the selection of mass exchangers, the main technological regimes and the parameters of their operation.

Key words: Production Cycle, Titanium Dioxide, Waste, Utilization, Mathematical Model